



Effect of FeCl_3 on sulfonamide removal and reduction of antimicrobial activity of wastewater in a photocatalytic process with TiO_2

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ABSTRACT

The aim of the study was to investigate the degradation of sulfonamides (SNs) in real wastewater samples using photocatalytic processes performed in the presence of a commercial TiO_2 catalyst (Degussa Aeroxide P25), FeCl_3 and a $\text{TiO}_2/\text{FeCl}_3$ mixture. The dynamics of the photodegradation of a mixture containing sulfadiazine, sulfamethoxazole and sulfathiazole in distilled water and in synthetic, municipal (raw and after treatment) wastewater, in wastewater from septic tank and in landfill leachate were compared during the study. The changes in the antimicrobial activity of the samples containing SNs and the photodegradation products were also assessed using the MARA[®] test.

It was observed that the photocatalytic degradation rate of SNs was primarily dependent on the environmental pollution degree, the catalytic system composition and pH values. In a landfill leachate the SNs photodegradation practically did not proceed. The inhibitors of the process were primarily soluble wastewater components.

The decomposition products of the SNs did not cause an increase in the antimicrobial activity of the reaction medium. The highest effectiveness for the photodegradation of SNs was obtained using the mixture containing TiO_2 ($\sim 0.5 \text{ g l}^{-1}$) and FeCl_3 ($\sim 0.5 \text{ mmol l}^{-1}$) at pH ~ 3.0 . The activity of this catalyst system estimated based on the half-life values of the SNs in the investigated samples were approximately 4.5 times greater than that in the presence of TiO_2 alone. Its high activity at pH ~ 3 primarily resulted from the decrease in the dissociation degree of other wastewater components in acidic medium, rather than the synergism of both photocatalyst components.

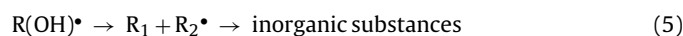
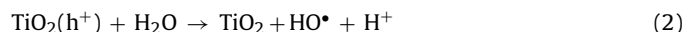
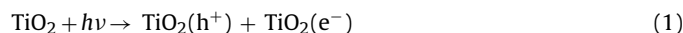
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1. Introduction

One of the negative consequences of the current development of civilisation is an increase in amount of anthropogenic pollutants that are introduced into the environment. An example of a substance whose excessive, quickly growing consumption has drawn special concern in recent years are synthetic antibacterial drugs, e.g., sulfonamides (SNs), which are used in medical and veterinary applications [1–5]. The risks related to their presence in the environment are primarily associated with a high probability of organisms developing drug resistance [3–5].

Some experts consider that routinely used wastewater treatment technologies and solid wastes utilisation are sufficient to alleviate the risks to human health from the SNs contained in them [5–7]. According to others, up to 80% of used SNs enter the environment [8]. However, the fact that there are trace amounts of SNs commonly present in soils, surface waters and even in abyssal

waters is undisputable. The data obtained from regular monitoring of the environment confirm the high frequency of such contaminations [2,3,5,9]. It is possible that SNs do not undergo efficient biodegradation in the environment [5]. For these reasons, effective methods for eliminating SNs from wastewater have been intensively investigated in recent years [10,11]. Scientists have high expectations for the use of advanced oxidation processes (AOPs), especially ozonation [10–13] and photocatalysis [11–22]. Hydroxyl (HO^\bullet) and superoxide radicals ($\text{O}_2^{\bullet-}$) generated during these processes oxidise organic contaminations, thereby leading to their decomposition. An example schematic of such a process is presented below:



where R means organic substances.

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It is also possible to directly oxidise organic compounds adsorbed on the TiO₂ surface, for example:

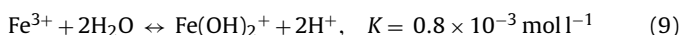
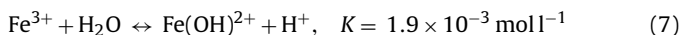


In this case, it is theoretically possible to obtain a much higher quantum efficiency for the degradation process [23].

The photocatalytic process may result in a complete mineralisation of the organic substances. However, it has been noted that the intermediate products from the photodegradation of SNs may be easier to biodegrade and less ecotoxic than the initial SNs [24]. Because of this fact and due to economic considerations, the use of photocatalysis for the preliminary decomposition of drugs followed by biodegradation for the complete mineralisation of the formed intermediate products may be more suitable. The combination of both processes should, without high costs, lower the degree of contamination with organic substances and the toxicity and antimicrobial activity of wastewater containing antibiotics [24].

Many of the cited papers present the results of studies on the photocatalytic degradation of SNs using commercial TiO₂ (P25-Degussa) as a catalyst [13–17,19,20]. The effectiveness of this catalyst may be considerably improved through the addition of Fe³⁺ salts, e.g., FeCl₃, to the reaction medium [21,25].

There are many reports that confirm the photocatalytic activity of Fe³⁺ salts [18,19,27–31]. In aqueous environments, the Fe³⁺ ion undergoes a successive cationic hydrolysis [26,27,30,31]:



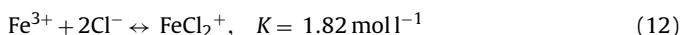
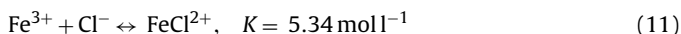
To simplify Eqs. (7)–(9), the water ligands coordinated to the Fe³⁺ ion were omitted. Among the abovementioned hydrolysis products, the Fe(OH)²⁺ ion has the highest photocatalytic activity. During irradiation, these ions generate HO• radicals [19,21,26,27,32,33]:



According to Baxendale and Magee [32], the quantum yield of this reaction can be greater than 30%. Depending on the initial concentration of the Fe salt, the concentration of the Fe(OH)²⁺ ion is at its maximum at a pH value between 3 and 4 [26,27,31].

The Fe₂(OH)₂⁴⁺ ions formed during the long term storage of aqueous solutions of Fe³⁺ salts or in solutions with high concentration of Fe salts have a significantly lower photocatalytic activity [26].

Additionally, Fe³⁺ ions may also form photochemically active coordination compounds with other inorganic ligands, such as Cl[−] [27,30,34]:



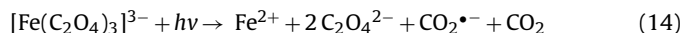
During irradiation, these chloride complexes can generate Cl• radicals with a quantum yield of 47% [34,35]:



However, in the opinion of some researchers, at low concentrations of chloride ions, the effect of the chlorine radicals on the photodegradation of organic compounds in the presence of Fe salt is not observed [27,33,36]. The organochlorine compounds were not detected in the photodegradation products of SNs degraded in the presence of FeCl₃ [19].

Iron ions (Fe³⁺) may also form highly photochemically active coordination compounds with some organic ligands. During

irradiation, electron transfer from the ligand to the Fe³⁺ ion is observed [26,37,38], e.g.:



By analysing the photochemical activity of the TiO₂/FeCl₃ mixture, Mestankova et al. [26] have observed that the photocatalytic degradation rate of Manuron in the presence of TiO₂/FeCl₃ is proportional to the concentration of Fe(OH)²⁺ ions. In turn, Zhang et al. [21] have demonstrated that the efficiency of HO• generation is greater in the presence of the TiO₂/FeCl₃ mixture than with TiO₂ alone. Therefore, the simultaneous use of TiO₂ and FeCl₃ causes an increase in the photocatalytic reaction rate because of synergistic effects.

Another possible reason for the enhanced activity is that in the mixture with TiO₂, the Fe³⁺ ion may also function as an acceptor for electrons in an excited state in the TiO₂ conduction band:



This process can limit possible recombinations of the excited electron–hole pairs, thereby favouring an increased generation efficiency of HO• radicals. However, the Fe²⁺ ions formed during photochemical reactions do not possess photocatalytic properties and do not intensify the process performed in the presence of TiO₂ [18,21]. According to Wang et al., reaction (15) leads to a reduction in the effectiveness of O₂^{•−} radical generation in reaction (3) and, as a consequence, may lead to a decrease in the photodegradation efficiency [39].

The products from the hydrolysis of Fe³⁺ ions are adsorbed onto the surface of TiO₂ crystals [21,40]. Therefore, the addition of Fe³⁺ salts can increase the efficiency of the photocatalytic process performed in the presence of TiO₂ by increasing the adsorption of organic substrates on the modified photocatalyst surface [21].

All of the studies described above were performed only in distilled water. The aim of our study was to use the photocatalytic process led in the presence of commercial TiO₂, FeCl₃ and a TiO₂/FeCl₃ mixture for the degradation of SNs added to real wastewater. We also aimed to determine the influence of the pH, concentration of the SNs, type of contaminants in the wastewater and the composition of the selected photocatalytic system on the investigated photocatalytic process. Based on the obtained results, we propose a mechanism for the photocatalytic process performed in the presence of TiO₂/FeCl₃ in wastewater.

2. Experimental

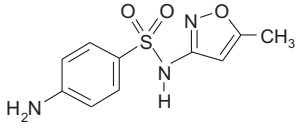
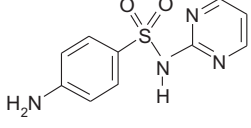
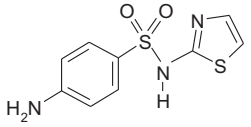
2.1. Reagents

General characteristics of the investigated SNs are presented in Table 1.

All of the investigated SNs were of analytical grade and were manufactured by Sigma. Immediately before each of the experiments, the weighed mixture of these SNs was added to the wastewater samples or distilled water and thoroughly mixed. The molar ratios of the SNs in the investigated samples are presented in Table 1. The concentration of sulfamethoxazole (SMX) in the samples was two-times greater than that sulfadiazine (SDZ) or sulfathiazole (STZ). This greater concentration of SMZ results from the fact that the concentration and frequency of SMX in environmental matrices are generally considerably higher than those of other SNs [5].

TiO₂ (Aeroxide® TiO₂ P25, Evonic Degussa GmbH) and FeCl₃ (pure for analysis; POCH s.a., Poland) were used as the components of the photocatalytic system. An HCl solution (pure for analysis; POCH s.a., Poland) was used to adjust the pH of the samples. In our

Table 1
The characteristics of investigated SNs.

Name of sulfonamides	Abbr. in text	Chemical structure	CAS No.	pK _{a1} ^a	pK _{a2} ^a	k _{OH} ^b (1 mol ⁻¹ s ⁻¹)	Molar ratio of SNs	t _R ^c (min)
Sulfamethoxazole	SMX		723-46-6	1.83	5.57	(5.8 ± 0.2) × 10 ⁹	0.50	7.49
Sulfadiazine (natrium salt)	SDZ		547-32-0	2.10	6.28	3.7 × 10 ⁹	0.25	3.48
Sulfathiazole (natrium salt)	STZ		144-74-1	2.08	7.07	(7.1 ± 0.2) × 10 ⁹	0.25	12.66

^a $\text{SNH}_2^+ \xrightleftharpoons{K_{a1}} \text{SNH} \xrightleftharpoons{K_{a2}} \text{SN}^-$ [41].

^b Reaction rate constant for SNs with HO• [42,43].

^c Retention time for mobile phase flow 1.0 ml min⁻¹, the detailed data on the mobile phase is in Section 2.5.

previous study, no significant changes in the SN concentration in samples irradiated only in the presence of HCl were observed.

2.2. Wastewater samples

The wastewater samples were derived from a municipal sewer system (municipal wastewater), a mechanical–biological wastewater treatment plant (effluent), a household septic tank and from a municipal landfill. Characteristics of the wastewater samples are presented in Table 2. After collection, all of the samples were stored at a temperature below −18 °C. Before starting the experiment, the samples were stored at room temperature for 24 h and then aerated for 1 h.

To limit the influences of meteorological conditions on the obtained results, the municipal wastewater and effluent samples were collected three times (in autumn after longstanding rainfalls, after a period without rain and in the winter). The averaged results obtained for all municipal wastewater and effluent samples are presented in this paper.

The synthetic wastewater was prepared based on ISO 9887:1992(E) (Table 3).

2.3. Wastewater coagulation

The wastewater samples (before the addition of SNs) were coagulated in 250 ml beakers. 4 ml of FeCl₃ solution (0.1 mol l⁻¹) was added to 200 ml of wastewater as a coagulant. The samples were simultaneously mixed with compressed air. The mixing was stopped after 5 min, and the samples were left for sedimentation (for 30 min). The supernatant was used in a subsequent part of the experiment.

2.4. Irradiation

Solid TiO₂ and/or concentrated FeCl₃ solution (0.1 mol l⁻¹) was added to the samples (100 ml) before the beginning of the irradiation. The pH of the samples was adjusted by adding appropriate amounts of the concentrated HCl solution. The mixture was then homogenised for 30 min in the dark using magnetic stirrers.

The irradiation was performed in open crystallisers (volume: 500 ml, exposed surface: 102 cm², thickness of the irradiated solution: ~1 cm) using four UV lamps (Philips TL-40 W/05 at

λ_{max} 366 nm). The concentration of radiation measured using a Quantum-photo-radiometer DO9721 (Delta OHM) was 5.3 and 9.3 W m⁻² for UVa and VIS, respectively. During the irradiation, the samples were mixed and had free contact with air. The sample temperature was 21–24 °C.

2.5. Analytical methodology

The samples that were collected before and during the irradiation were centrifuged (30 min, 4000 RPM). Then, the concentration of SNs was determined using the HPLC method (column Supelcosil Suplex pKB-100 LC-18, 5 μm, 250 mm × 4.6 mm; detector Waters TAD 486, λ = 254 nm; mobile phase K₂HPO₄ pH 8.2/CH₃CN in the ratio 95:5). The determined retention times for specific SNs are presented in Table 1.

2.6. Determination of antimicrobial activity of the samples

Example studies for the antimicrobial activity were conducted for SMX (C₀ = 0.5 mmol l⁻¹) and the products of its photodegradation in distilled water. The concentration of SMX was established based on the value of minimum toxic concentrations of this sulfonamide in relation to the test organisms listed below. To remove the Fe ionic compounds that may affect the growth of the test microorganisms, the preparation of acidic samples (containing Fe salts) relied on their neutralisation to pH 6–6.5 and centrifugation (20 min, 4000 rpm). Then, the growth of the test organisms in comparison to the control samples was assessed. The MARA[®] test described by Wadhia et al. [44] was used in these experiments. This test provides an objective assessment of antimicrobial activity changes of a sample based on the changes in growth of *Microbacterium* spp, *Brevundimonas diminuta*, *Citrobacter freundii*, *Comamonas testosteroni*, *Enterococcus casseliflavus*, *Delftia acidovorans*, *Kurthia gibsonii*, *Staphylococcus warneri*, *Pseudomonas aurantiaca*, *Serratia rubidaea* bacteria and *Pichia anomalia* yeasts [45].

2.7. Results elaboration

The results from the photocatalytic degradation of the SNs were assessed based on the results obtained of two simultaneously irradiated, identical samples. The only exception was the half-life

Table 2

The characteristics of the used wastewater samples (without SNs).

	Municipal wastewater (3 samples)	Effluent (3 samples)	Wastewater from septic tank	Landfill leachate	Synthetic municipal wastewater
Coordinates of sampling locations	50.303609, 19.204316	50.301583, 19.202657	50.371094, 19.038168	50.375159, 19.058467	–
pH	7.58–7.92	7.10–7.66	8.69	8.37	6.93
COD (mg O ₂ l ^{−1})	611–902	137–774	820	>2000	295
BOD ₅ (mg O ₂ l ^{−1})	152–199	60–89	368	360	n.d.
Conductivity (mS cm ^{−1})	0.508–1.789	1.204–1.722	2.560	8.250	0.420
Turbidity (FTU)	40–145	4–50	352	n.d.	2
Abs _{254nm}	0.380–0.752	0.196–0.346	1.77	n.d.	0.268

n.d. – no data.

Table 3

Chemical composition of the synthetic municipal wastewater.

Chemicals	CAS No.	Manufacturer	Purity or product information	Concentration (mg l ^{−1})
Peptone from animal proteins	73049-73-7	Fluka	For microbiology no cat. 77180	160
Meat extract	–	Fluka	For microbiology no cat. 70164	110
Urea	57-13-6	Sigma–Aldrich	For molecular biology	30
K ₂ HPO ₄	7758-11-4	POCH s.a. (Poland)	Pure for analysis	28
NaCl	7647-14-5	POCH s.a. (Poland)	Pure for analysis	7
CaCl ₂ ·2H ₂ O	10035-04-8	POCH s.a. (Poland)	Pure for analysis	4
MgSO ₄ ·7H ₂ O	10034-99-8	POCH s.a. (Poland)	Pure for analysis	2

values ($T_{1/2}$) of the SNs in the municipal wastewater and effluent after WWTP (Figs. 4 and 5). In these cases, the mean values were calculated from the results obtained during the measurement series with three samples, which were collected from the same location but at different times (see Section 2.2).

The degree of removal for particular SNs was determined based on the following equation:

$$Y_i = 100 \cdot \left(1 - \frac{C_i}{C_0}\right) \quad (16)$$

where Y_i is the degree of SDZ, SMX or STZ removal (%), C_0 is the initial concentration of SDZ, SMX or STZ, and C_i is the final concentration of SDZ, SMX or STZ (in the sample).

The weighted average of the removal of SNs (Y_{SNs}) was calculated according to the following equation:

$$Y_{SNs} = \sum x_i Y_i \quad (17)$$

where x_i is the mole fraction of the examined SNs (Table 1).

The value of the pseudo-first-order reaction rate (k) constant was determined from the slope of the linear equation:

$$\ln \frac{C_i}{C_0} = -k_i t + b \quad (18)$$

where t is the irradiation time and b is the intercept of the linear equation.

The $T_{1/2}$ values were determined using two methods. Firstly, with the graphical method, they were obtained from the relationship plot:

$$Y_i = f(t) \quad (19)$$

Secondly, they were calculated based on the equation:

$$T_{1/2} = \frac{\ln 2}{k_i} \quad (20)$$

In the case of reactions proceeding with a very low rate, the $T_{1/2}$ value was estimated by extrapolating the k_i value (Eq. (20)).

3. Results and discussion

3.1. Preliminary studies of SNs degradation in distilled water environment

The results from the photocatalytic degradation studies of SNs conducted so far by our team and the available literature concerning this subject indicate that these drugs undergo photocatalytic degradation in aqueous solutions. In the experiment described below, the mixture of investigated SNs ($\Sigma C_0 = 0.1 \text{ mmol l}^{-1}$) in distilled water was irradiated with UVa radiation for 60 min in the presence of TiO₂ (0.5 g l^{−1}) and/or FeCl₃ (1.0 mmol l^{−1}). The concentrations used were established based on previous experiments [19]. Fig. 1 presents the dynamics of the photocatalytic degradation for a sum of the SNs calculated based on Eq. (17). The pH of the

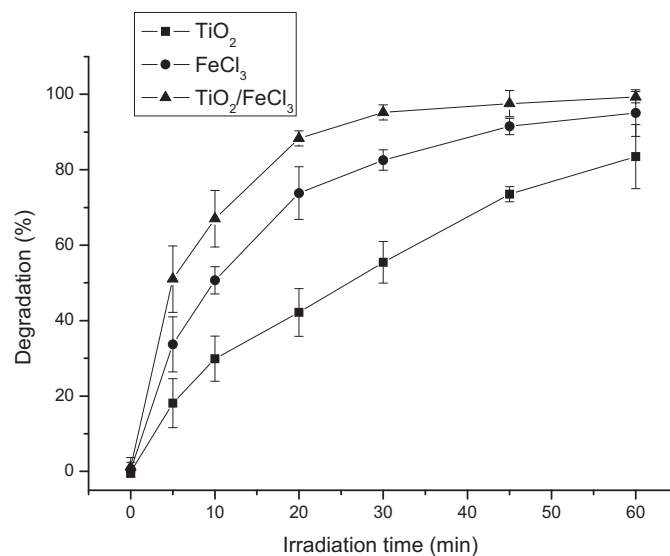


Fig. 1. The dynamics of the weighted average of photodegradation of SNs ($\Sigma C_0 = 0.1 \text{ mmol l}^{-1}$) in distilled water in the presence of TiO₂ (0.5 g l^{−1}) and/or FeCl₃ (1.0 mmol l^{−1}).

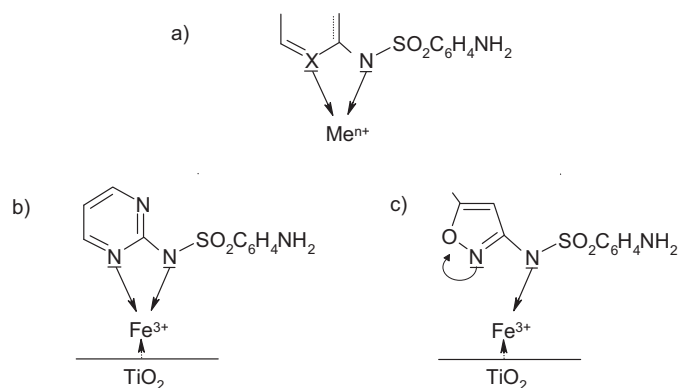


Fig. 2. The schematic formation of coordination bonds between SNs and metal ions. Binding of STZ particles should occur similarly to that for SDZ (b).

samples was not adjusted. Detailed results obtained for SMX, SDZ and STZ are presented in Table 4.

The results indicated that the rate of SDZ and STZ degradation under the used conditions, in the presence of the TiO₂/FeCl₃ mixture, is considerably greater than that in the presence of TiO₂ or FeCl₃ alone (Table 4). The rates of SMX degradation in the presence of TiO₂/FeCl₃ and FeCl₃ were similar. In practice, the application of the TiO₂/FeCl₃ mixture as a photocatalyst may be more expensive than FeCl₃ alone. However, considering the obtained high mean efficiency for the removal of SNs (>70%), the application of TiO₂/FeCl₃ rather than FeCl₃ alone is more favourable (Fig. 1). As a result, under the used conditions, the required irradiation time was shortened from ~18 to 11 min (Fig. 1). Zhang et al. [21] have observed that the main reason for the increased photodegradation rate of SDZ in the presence of TiO₂/FeCl₃ is a higher chemisorption efficiency of this SN than in the case TiO₂ alone. This higher chemisorption results from the modification of the catalyst surface by Fe³⁺ ions. According to Tommasino et al. [46], SNs form coordination bonds with metal ions, as shown in Fig. 2a.

Fe³⁺ ions (or products from their partial hydrolysis) adsorbed on the TiO₂ surface can form weak coordination bonds with SNs (Fig. 2 a and b). According to Eq. (6), this process should cause an increase in the degradation efficiency of SNs on the TiO₂ surface. In the case of SMX, the high electronegativity of the oxygen located next to the nitrogen atom in the heterocyclic ring may shift the non-binding electron pair of nitrogen and prevent the formation of other coordination bonds (Fig. 2c). This fact may explain the smaller effect of the FeCl₃ addition on SMX than SDZ and STZ degradation. During the photodegradation of SDZ and STZ in the presence of TiO₂/FeCl₃, the more probable explanation for the increased efficiency is a participation of direct charge-transfer processes and reaction with radicals on the surface of the catalyst particles. However, SMX will likely be more oxidised by radicals generated in the homogeneous phase.

In the case of photocatalysts containing Fe³⁺ salts, a negative effect is lowering their activity during the photocatalytic reaction. That effect may be caused by a reduction of Fe³⁺ to Fe²⁺ (Eqs. (7), (13)–(15)). Fe²⁺ salts are strong inhibitors of the photodegradation of SNs in the presence of TiO₂ [18,21]. As a consequence, the order of the photocatalytic reaction may be changed [18]. Therefore, the two values of *T*_{1/2} are presented in Table 4; the first one was calculated based on the pseudo-first-order reaction rate constant (Eq. (20)), and the real values were read from the plot (Eq. (19)). Note that the differences between these values do not influence the qualitative description of the investigated processes (Table 4).

One of the most important purposes for treating wastewater that contains antibiotics is to reduce their antibacterial activity. According to Trovo et al., the toxicity of advanced oxidation

Table 4
The results of photocatalytic degradation of SNs in distilled water.

Substrate	TiO ₂ (0.5 g l ⁻¹) pH = 4.8 ± 0.5				FeCl ₃ (1.0 mmol l ⁻¹) pH = 3.08 ± 0.05				TiO ₂ (0.5 g l ⁻¹) and FeCl ₃ (1.0 mmol l ⁻¹) pH = 3.10 ± 0.08			
	Reaction time ^a (min)	<i>k</i> (min ⁻¹)	<i>T</i> _{1/2} ^b (min)	<i>T</i> _{1/2} ^c (min)	Reaction time ^a (min)	<i>k</i> (min ⁻¹)	<i>T</i> _{1/2} ^b (min)	<i>T</i> _{1/2} ^c (min)	Reaction time ^a (min)	<i>k</i> (min ⁻¹)	<i>T</i> _{1/2} ^b (min)	<i>T</i> _{1/2} ^c (min)
STZ	0–60	0.033 ± 0.002	21.0	18.1	0–30	0.090 ± 0.002	7.7	6.2	0–10	0.378 ± 0.015	1.8	2.2
SMX	0–60	0.029 ± 0.003	23.9	21.9	0–45	0.074 ± 0.001	9.3	8.4	0–30	0.087 ± 0.003	8.0	8.3
SDZ	0–60	0.019 ± 0.001	37.3	37.7	0–45	0.033 ± 0.006	21.3	19.9	0–30	0.109 ± 0.007	6.4	5.8
SN ^d	0–60	0.029 ± 0.001	24.1	23.8	0–30	0.064 ± 0.003	10.8	9.3	0–20	0.124 ± 0.015	5.6	4.9

^a Results obtained for the reaction time were used to determine the *k* values according to the pseudo-first order kinetics.

^b Calculated from Eq. (20).

^c Determined by the graphical method (Section 2.7).

^d Values determined on a weighted average of photodegradation results (Section 2.7, Eq. (10)).

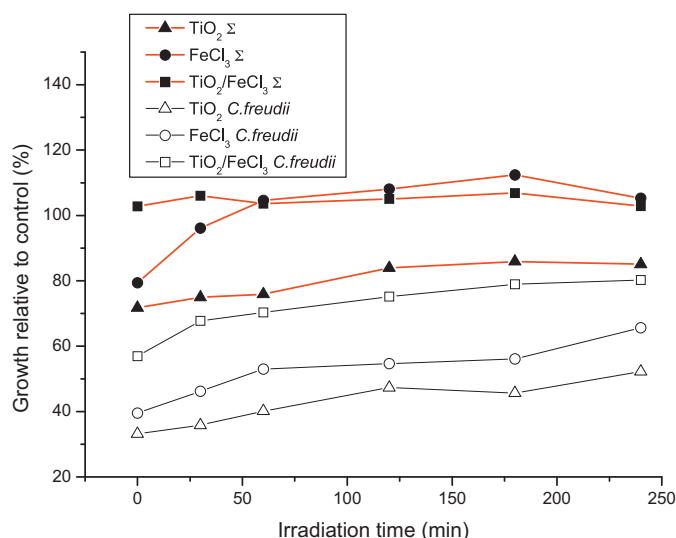


Fig. 3. The changes of antimicrobial activity of SMX solution ($C_0 = 0.5 \text{ mmol l}^{-1}$) during the photocatalytic processes.

products of SMX against *Vibrio fischeri* is higher than the toxicity of an initial SN [47]. However, in our opinion, the result of this test cannot be fully reliable for terrestrial ecosystems because *V. fischeri* originates from marine environments.

Fig. 3 presents the dynamics of changes in the antimicrobial activity of samples containing SMX ($C_0 = 0.5 \text{ mmol l}^{-1}$) against the selected microorganisms characteristic for different ecosystems [45]. After 240 min of irradiation in the presence of TiO_2 , FeCl_3 and $\text{TiO}_2/\text{FeCl}_3$, the samples contained 27, 28 and 6% of the initial amount of SMX, respectively.

It was observed that, independently of the catalyst used, the changes in the growth of the microorganisms, and therefore the antimicrobial activity of samples, before and after irradiation were small (Fig. 3). This observation likely results from the fact that most of these microorganisms did not exhibit any susceptibility against SMX at a concentration of $\leq 0.5 \text{ mmol l}^{-1}$. However, against more susceptible strains, e.g., *C. freundii*, the antimicrobial activity of samples after photocatalytic reaction clearly decreased with an increase in irradiation time (Fig. 3). Recapitulating, in our opinion, the products formed from the decomposition of SNs do not cause any adverse increase in the antimicrobial activity of the reaction medium.

3.2. Degradation of SNs in various samples

It was observed that the photolysis and adsorption of SNs under the used conditions were insignificant for the investigated photodegradation processes. Fig. 4 presents the weighted average of the $T_{1/2}$ values obtained during the photocatalytic degradation of the investigated SNs ($\Sigma C_0 = 0.1 \text{ mmol l}^{-1}$) added to distilled water, synthetic wastewater and real environmental samples (Table 2). The pH of the samples irradiated in the presence of FeCl_3 and $\text{TiO}_2/\text{FeCl}_3$ was adjusted to ~ 3 . HCl solution in amounts of 2–13 and 2–12 mmol l^{-1} , respectively, was added to the samples to adjust the pH. The pH of the samples irradiated in the presence of TiO_2 was not corrected. The samples were irradiated for a maximum of 240 min; therefore, the $T_{1/2}$ values that exceeded 240 min were estimated using the extrapolation method. In the case of the landfill leachate, the degradation of the SNs in the presence of FeCl_3 was too slow to determine the reliable $T_{1/2}$ value.

It was observed that the photodegradation rate of SNs in wastewater was significantly lower than that in distilled water, which was consistent with our expectations. Therefore, the

determined $T_{1/2}$ values of SNs in the wastewater were considerably higher. Independent of the catalyst used, higher degrees of wastewater contamination (higher COD value – Table 2) resulted in slower degradation of the SNs. In the landfill leachate in the presence of FeCl_3 , the decrease in the SN concentration during irradiation was barely observable (Fig. 4). Municipal wastewater contains considerably greater amounts of contaminations other than SNs. These substances (e.g., sugars, fatty acids and amino acids) may also be substrates for the photocatalytic process and can therefore compete with the SNs [48]. Furthermore, these substances are able to bind with the catalyst forming both agglomerates with TiO_2 , and stable, complex or insoluble compounds with Fe^{3+} . In the case of wastewater of a high turbidity (from the septic tank), the low reaction rate may also be caused by shadowing of the photocatalyst particles with suspensions. The high conductivity of the wastewater (Table 2) suggests that they may contain significant amounts of inorganic mobile anions, such as Cl^- , CO_3^{2-} , SO_4^{2-} , PO_4^{3-} , and NO_3^- , and in the case of poorly aerated sewage, the presence of S^{2-} ions should be expected. The abovementioned ions can significantly affect the distribution of hydroxyl radicals in the process:



As a consequence, it is expected that these anions at high concentrations can decrease the reaction rate that simultaneously occurs between HO^\bullet radicals and SNs. This expectation was confirmed by experimental data summarised in the paper by Aguedach et al. [49]. According to Lair et al. [50], inorganic anions can also have negative effects on the adsorption of organic compounds on the TiO_2 surface. However, Hu et al. [15] have reported that the presence of carbonate or bicarbonate ions can intensify the photodegradation of SNs. The authors explain that aniline derivatives (including SNs) undergo reactions with $\text{CO}_3^{\bullet-}$ radicals according to second order kinetics.

Except for the landfill leachate, the lowest values of the $T_{1/2}$ of SNs were obtained in the presence of the $\text{TiO}_2/\text{FeCl}_3$ mixture. These values were 2–5 times lower than in analogous experiments with the use of FeCl_3 alone, and 2–7 times lower than in the case of TiO_2 alone. This result indicates that the $\text{TiO}_2/\text{FeCl}_3$ mixture in wastewater (similarly in distilled water) is considerably more photocatalytically active compared to its individual components. The reasons discussed in the literature for an increased TiO_2 activity in the presence of Fe^{3+} were mentioned in the introduction. The reason for the increased activity that is most often given is an intensification of the HO^\bullet radicals generated as a result of synergism [21,26].

Fig. 5 presents the $T_{1/2}$ values obtained for SDZ, SMX and STZ that were irradiated in various samples in the presence of $\text{TiO}_2/\text{FeCl}_3$ only. The reciprocal proportions of the photodegradation rate of SNs in wastewater (except landfill leachate) were similar to those described for distilled water as reaction medium (Table 4). Among the investigated SNs, both in distilled water and in wastewater, their susceptibility to photocatalytic degradation increases in the following order: $\text{SMX} < \text{SDZ} < \text{STZ}$. This result is not consistent with the activity series of particular SNs in a reaction with HO^\bullet radicals (Table 1). On the contrary, as a result of reactions performed in the presence of TiO_2 or FeCl_3 only, the susceptibility of SNs to photodegradation increased in the series of $\text{SDZ} < \text{SMX} < \text{STZ}$, which is in accordance with their susceptibility to react with HO^\bullet radicals. This result may indicate that a reaction without the participation of HO^\bullet radicals has a significant or predominating effect on the photocatalytic process in the presence of $\text{TiO}_2/\text{FeCl}_3$. Therefore, the generation of these radicals is most likely not due to the stage-limiting photodegradation of SNs in the presence of $\text{TiO}_2/\text{FeCl}_3$.

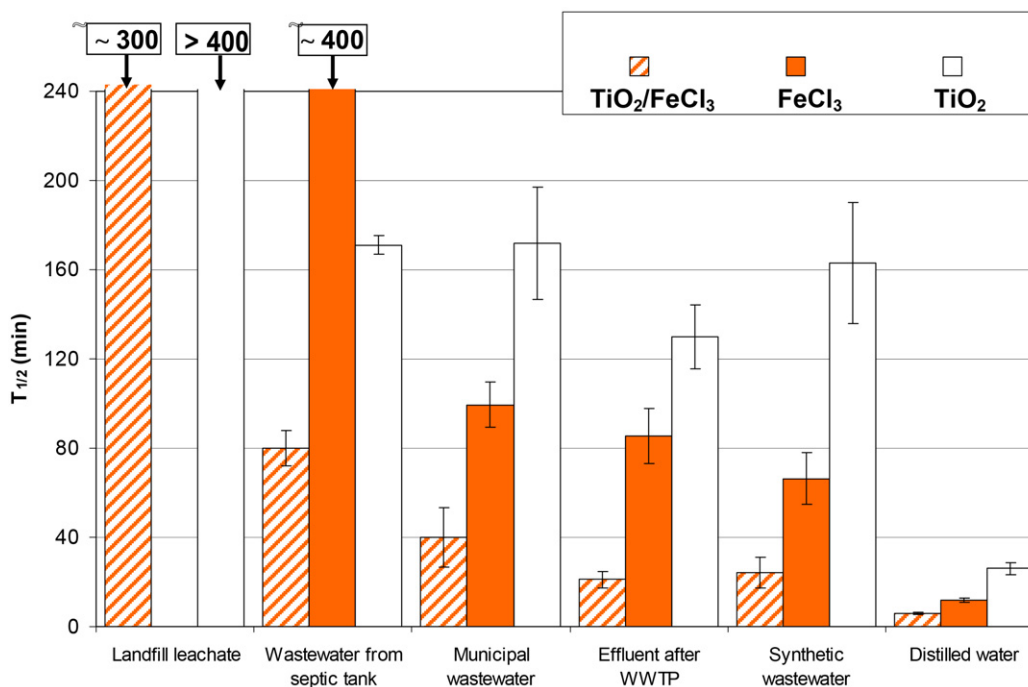


Fig. 4. The weighted averages of $T_{1/2}$ values determined during irradiation of samples with SNs in the presence of TiO_2 (0.5 g l^{-1}) and/or FeCl_3 (1.0 mmol l^{-1}). The height of columns for landfill leachate is not in proportion to the actual size.

3.3. Effect of the conditions of photocatalytic degradation of SNs in municipal wastewater in the presence of $\text{TiO}_2/\text{FeCl}_3$

The $\text{TiO}_2/\text{FeCl}_3$ mixture was selected as the most effective photocatalyst for the degradation of SNs in wastewater. In the subsequent experiments, the effects of pH, concentration of the SNs, type of pollutants in the wastewater and composition of the selected photocatalytic system on the investigated photocatalytic process were examined in the presence of $\text{TiO}_2/\text{FeCl}_3$. To eliminate the discrepancies caused by the differences in properties of the

reaction medium (wastewater), one sample of municipal wastewater was used in each of the measurement series in all of the experiments described below.

3.3.1. Effect of the pH

The current studies have confirmed that the pH value has a significant influence on the photocatalytic process performed in distilled water in the presence of $\text{TiO}_2/\text{FeCl}_3$ [19,21,26]. Most of the papers cited describe a stepwise increase in the reaction rate in samples with a pH ~ 3 . In the solutions containing $\sim 1 \text{ mmol l}^{-1}$ of

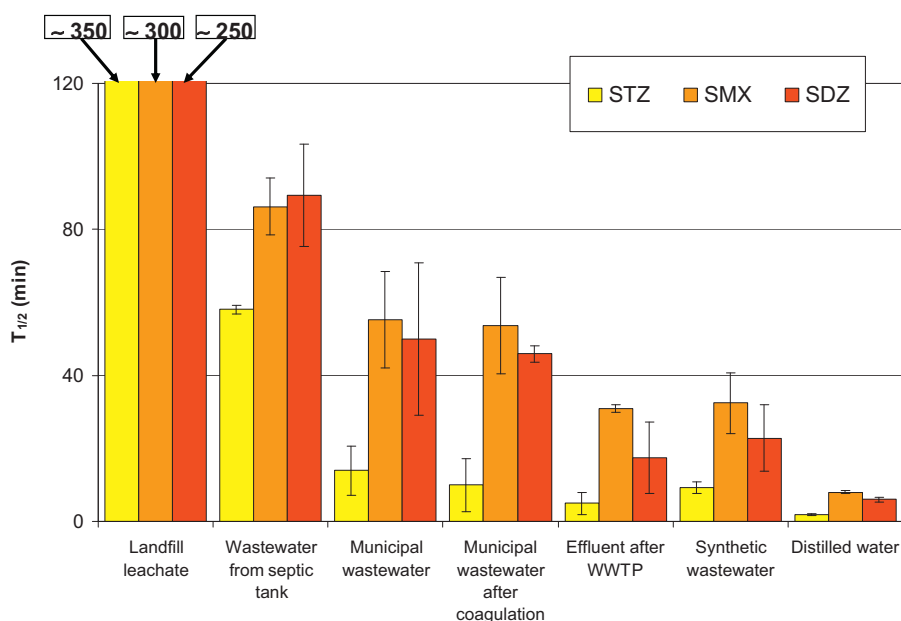


Fig. 5. The $T_{1/2}$ values of individual SNs determined during irradiation with TiO_2 (0.5 g l^{-1}) and FeCl_3 (1.0 mmol l^{-1}) mixture. The height of columns for landfill leachate is not in proportion to the actual size.

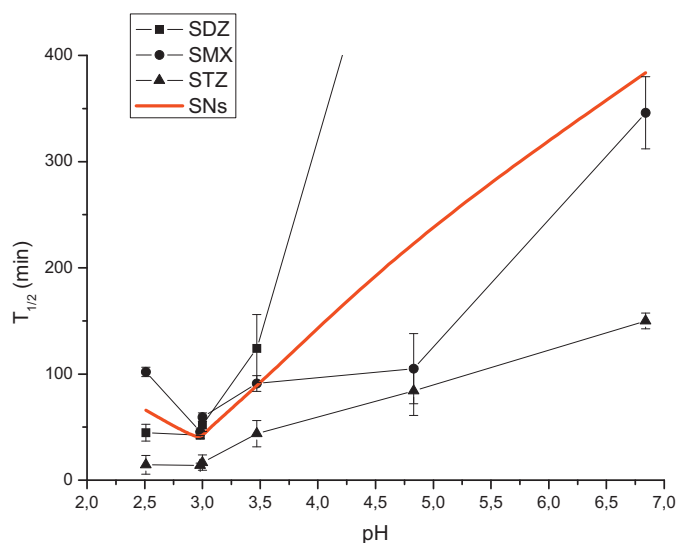


Fig. 6. Effect of pH on the photocatalytic degradation of SNs in wastewater in the presence of $\text{TiO}_2/\text{FeCl}_3$.

Fe^{3+} salts, the concentration of the photoactive $\text{Fe}(\text{OH})^{2+}$ ion also reaches a maximum at pH 3 [51]. This fact may indicate a significant participation of the $\text{Fe}(\text{OH})^{2+}$ ion in the initiation step of the photocatalytic process in model solutions.

The influence of the pH of the wastewater on the $T_{1/2}$ value of SNs ($\Sigma C_0 = 0.1 \text{ mmol l}^{-1}$) in the presence of TiO_2 (0.5 g l^{-1}) and FeCl_3 (1.0 mmol l^{-1}) mixture is presented in Fig. 6.

It was observed that the dynamics of changes in the $T_{1/2}$ values with the change of pH in wastewater had a distinct extreme at pH 3 only for SMX. SDZ and STZ underwent the fastest degradation at $\text{pH} \leq 3$, whereas the rate of SDZ degradation decreased rapidly with an increase in $\text{pH} > 3$ (Fig. 6). The above results confirm the observation described in Section 3.1 where the mechanism of SMX, SDZ and STZ degradation is different. Decreasing the pH from 3 to 2.5 caused a decrease in the $\text{Fe}(\text{OH})^{2+}$ concentration and, most likely, a decrease in the efficiency of HO^\bullet generation in the homogeneous process. In this pH range, a decrease in the photodegradation rate of SMX (differently than in the case of SDZ and STZ) was also observed. This observation may confirm the previously described assumption that HO^\bullet radicals are important for the degradation of SMX in the homogeneous phase. However, in the entire investigated range of pH values, the dynamics of changes of the discussed relationship were considerably lower than in the case of the photodegradation of SNs in distilled water in the presence of FeCl_3 alone [19]. Therefore, in our opinion, the reaction catalysed by the $\text{Fe}(\text{OH})^{2+}$ ion in wastewater contributed to the photodegradation of the SNs to a smaller degree (especially in the case of STZ).

Unfortunately, the fact that in wastewater with a natural pH (6–8), the photodegradation of SNs is considerably slower and is very unfavourable from the practical point of view because it requires their additional acidification.

3.3.2. Effect of initial FeCl_3 concentration

The effect of the initial FeCl_3 concentration ($0\text{--}3.0 \text{ mmol l}^{-1}$) in the mixture with TiO_2 (0.5 g l^{-1}) on the value of $T_{1/2}$ of the SNs ($\Sigma C_0 = 0.1 \text{ mmol l}^{-1}$) in wastewater is presented in Fig. 7. This figure also presents the effect of a decrease in pH (from 7.9 to 3) on the photodegradation of the SNs in the presence of TiO_2 alone.

During irradiation of the wastewater samples in the presence of TiO_2 only, a decrease in their pH from 7.9 to 3.0 caused a decrease in the $T_{1/2}$ value for SDZ, SMX and STZ by 48, 79 and 76%, respectively. At pH 3, the addition of FeCl_3 ($\leq 0.5 \text{ mmol l}^{-1}$)

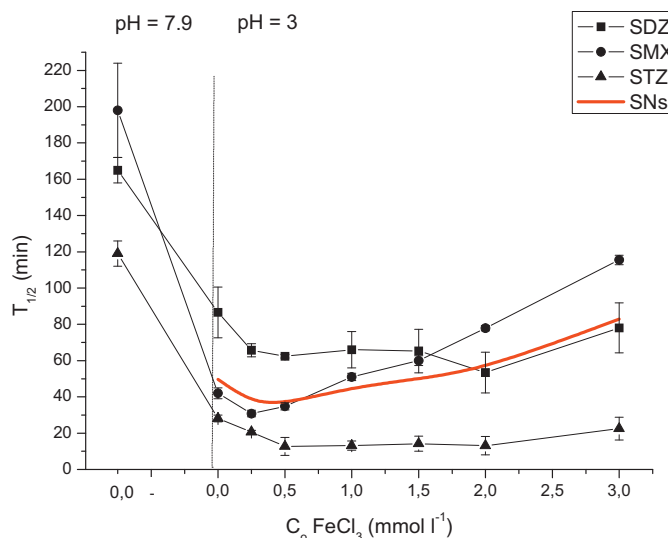


Fig. 7. Effect of the initial FeCl_3 concentration and the pH on the photocatalytic degradation of SNs in wastewater irradiated in the presence of TiO_2 and $\text{TiO}_2/\text{FeCl}_3$ mixture.

to TiO_2 caused a further decrease in the $T_{1/2}$ value for the SNs, approximately 27% on average (Fig. 7). For all of the investigated SNs, the minimum values of $T_{1/2}$ were observed at the FeCl_3 concentration range of $0.25\text{--}0.5 \text{ mmol l}^{-1}$. In the case of SDZ and STZ, a further increase in the FeCl_3 concentration from 0.5 to 2.0 mmol l^{-1} caused only a negligible change in the $T_{1/2}$ value. At concentrations greater than 2.0 mmol l^{-1} , FeCl_3 inhibited the photodegradation of these SNs. In the case of SMX, an increase in the FeCl_3 concentration $> 0.25 \text{ mmol l}^{-1}$ caused a monotonic decrease in the rate of its photodegradation (at a concentration $> 0.75 \text{ mmol l}^{-1}$, FeCl_3 was practically an inhibitor of the studied process).

According to the literature data, the rate of photocatalytic degradation of the selected SNs in distilled water in the presence of TiO_2 increased with an increase in acidity in the case of sulfisoxazole ($\text{pK}_{a1} = 1.6$) and sulfachloropyridazine ($\text{pK}_{a1} = 2.0$), whereas it decreased in the case of sulfanilamide ($\text{pK}_{a1} = 2.4$) and sulfapyridine ($\text{pK}_{a1} = 4.25$) [19,20]. Our current unpublished studies indicate that under analogous conditions, an increase in acidity causes a decrease in the photodegradation rate of SDZ and an insignificant increase in the photodegradation rates of SMX and STZ. HCl (used for adjusting the pH) does not exhibit photocatalytic properties.

As previously mentioned, in these wastewaters, the SNs concentration was considerably lower than that of, for example, detergents and the products from the partial degradation of fats. In acidic environments, these compounds are primarily present in their undissociated forms (they form hydrophobic particles). Furthermore, in the presence of Fe salts, these compounds and amino acids can form stable coordination compounds. Therefore, as a result of decreasing pH and adding of Fe salts, the adsorption of these components of wastewater on active centres of the photocatalyst (TiO_2) can be decreased. In this way, the majority of these centres can be used in the degradation of SNs.

In acidic environments, the concentration of weak acid anions is also significantly decreased. Therefore, the inhibitory effect induced, e.g., by the presence of trace amounts of S^{2-} ions can be decreased. However, the positive effect caused by the presence of carbonate and bicarbonate ions will simultaneously decrease [15].

The FeCl_3 added to the samples causes a significant decrease in their pH. This decrease is likely the main reason for the high rate of SNs photodegradation in wastewater in the presence of $\text{TiO}_2/\text{FeCl}_3$. The higher photocatalytic activity of $\text{TiO}_2/\text{FeCl}_3$ in comparison with TiO_2 alone at pH 3 indicates that the discussed process may also

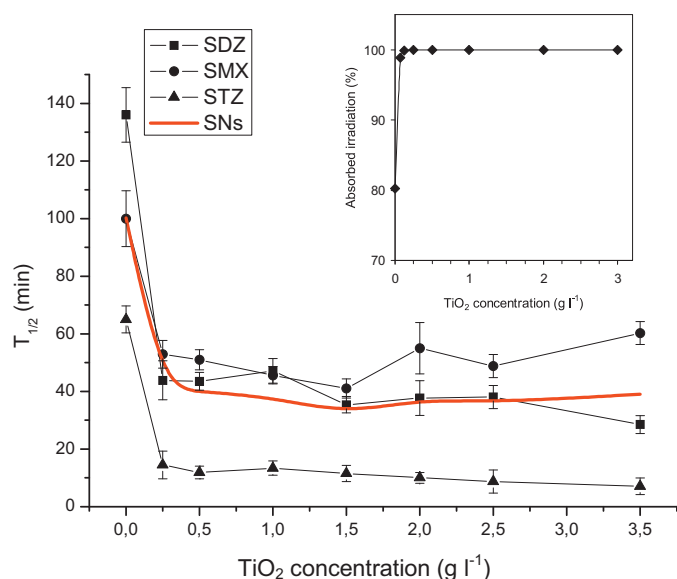


Fig. 8. Effect of TiO_2 concentration on the photocatalytic degradation of SNs in wastewater in the presence of $\text{TiO}_2/\text{FeCl}_3$.

be intensified by the $\text{Fe}(\text{OH})^{2+}$ ion. However, the influence of the ion on the final effect of SNs photodegradation is lower than that described by the increase in the acidity of the reaction medium.

The explanation for the inhibition of the photodegradation of SNs in wastewater with high FeCl_3 concentrations is more complicated. This phenomenon was not observed in distilled water, therefore, its reasons are likely associated with components in the wastewater.

Because the inhibition effect primarily concerns the SMX and not all of the investigated SNs proportionally, we suspect that it is not a result of catalyst shadowing by agglomerates of iron compounds and wastewater components. In distilled water, an increase in the FeCl_3 concentration increases the formation of less active photocatalytic dimers through the hydrolysis of Fe^{3+} ions [26]. It is not excluded that this process is the main cause of reduction in the photodegradation rate of SMX for $C_{\text{FeCl}_3} > 0.25 \text{ mmol l}^{-1}$.

It is significant from the practical point of view that the HCl dose required to decrease the pH of wastewater when the $\text{TiO}_2/\text{FeCl}_3$ mixture is used may be considerably lower than that required in the case of TiO_2 alone.

3.3.3. Effect of TiO_2 concentration

Fig. 8 shows the effect of the TiO_2 concentration on the $T_{1/2}$ value of the SNs ($\Sigma C_0 = 0.1 \text{ mmol l}^{-1}$) in wastewater irradiated in the presence of TiO_2 (0–3.5 g l^{-1}) and FeCl_3 (1.0 mmol l^{-1}) mixture. The pH of all of the irradiated samples was pH ~ 3 . The graph at the top of Fig. 8 shows the degree of absorption of radiation at λ 366 nm by the irradiated samples.

It was observed that a small addition of TiO_2 (0.25 g l^{-1}) to wastewater containing FeCl_3 considerably ($\sim 60\%$) decreased the $T_{1/2}$ value of all of the investigated SNs. Simultaneously, the absorption of radiation by the sample increased from approximately 80 to almost 100% (Fig. 8, internal plot). Therefore, the increase in the photocatalytic reaction rate in this case was considerably greater than the increase in the intensity of absorbed radiation. Because a reaction rate is proportional to the intensity of the radiation that excites the photocatalyst over a wide range [50], it should be assumed that the described catalytic effect is not associated with this phenomenon. This result confirms that in wastewater, the photocatalytic process occurring on the surface of TiO_2 has a

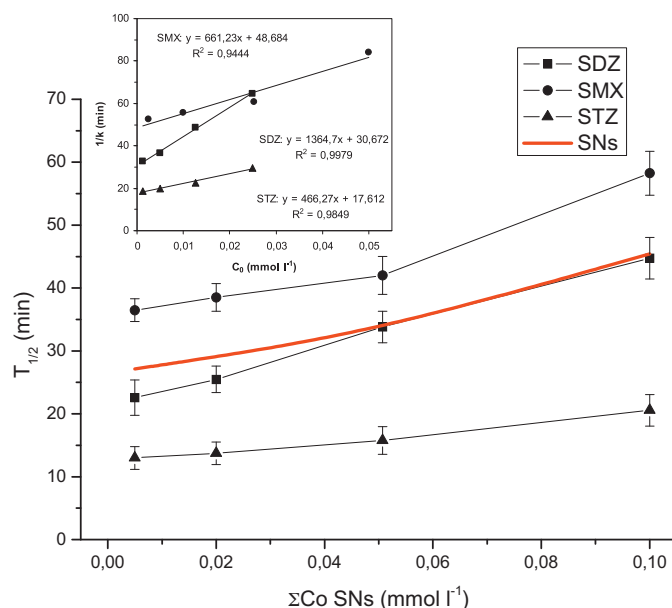


Fig. 9. Effect of the initial SNs concentration on their photodegradation in wastewater irradiated in the presence of $\text{TiO}_2/\text{FeCl}_3$.

considerably greater effect on the effectiveness of the photodegradation of SNs than the process catalysed with $\text{Fe}(\text{OH})^{2+}$ ions.

As mentioned, even a small addition of TiO_2 to the irradiated mixture resulted in the complete absorption of the radiation flux. Therefore, in accordance with these expectations, the further increase in the TiO_2 concentration from 0.25 to 3.5 g l^{-1} did not cause a significant increase in the photocatalytic reaction rate.

When omitting one of the results (SDZ; $C_{\text{TiO}_2} = 2.0 \text{ g l}^{-1}$), the most effective concentration of TiO_2 under the used conditions was $\sim 1.5 \text{ g l}^{-1}$. However, a six-fold increase in the TiO_2 dose (from 0.25 to 1.5 g l^{-1}) would cause an estimated lowering of mean value of $T_{1/2}$ of only approximately 25%, therefore, the concentration of TiO_2 of 0.5 g l^{-1} was used in the subsequent study.

3.3.4. Effect of suspensions and colloidal contaminations

The above results indicated that other wastewater components significantly influenced the rate of photocatalytic degradation of the SNs. These components are chemical substances present in a form of true solutions, colloidal solutions and suspensions. To determine which of the mentioned groups of substances has the largest effect on the photocatalytic process, wastewater samples were coagulated with FeCl_3 . As a result, a decrease in the pH (1.5 unit) and turbidity (71%) of the wastewater occurred. Mainly colloidal substances and suspensions were removed as a result of coagulation. After coagulation, SNs ($\Sigma C_0 = 0.1 \text{ mmol l}^{-1}$) were added to wastewater and samples underwent the photocatalytic process in the presence of the TiO_2 (0.5 g l^{-1}) and FeCl_3 (1.0 mmol l^{-1}) mixture. The pH of the samples was adjusted to 3. The obtained results were compared to those from wastewater that was not coagulated (Fig. 5).

It was observed that wastewater coagulation before the photocatalytic process practically did not affect the $T_{1/2}$ value of the SNs. Only in the case of STZ was a decrease in the $T_{1/2}$ ($\sim 28\%$) value observed (Fig. 5). This result indicates that colloidal substances and suspensions practically did not influence the photocatalytic reaction. Therefore, other components soluble in wastewater have a significant effect on slowing the photocatalytic process.

3.3.5. Influence of an initial SNs concentration

Fig. 9 presents the relationship between the value of $T_{1/2}$ of SNs and their initial concentration in wastewater. Samples were irradiated in the presence of the TiO_2 (0.5 g l^{-1}) and FeCl_3 (1.0 mmol l^{-1}) mixture at pH ~ 3 .

Note that an increase in the initial concentration of SNs from 0.05 to 0.1 mmol l^{-1} caused a negligible decrease in the rate of their photodegradation. The obtained results were characterised by good fit to a linear form of the Langmuir–Hinshelwood equation (Fig. 9, internal plot):

$$\frac{1}{k} = \frac{C_0}{k^*} + \frac{1}{k^*K} \quad (22)$$

where k^* – intrinsic reaction rate constant and K is the Langmuir–Hinshelwood adsorption constant.

According to the Langmuir–Hinshelwood theory, when trace amounts of SNs are present in wastewater, the time required for their photocatalytic degradation should be expected to be shortened.

4. Conclusions

The photocatalytic degradation of SNs in wastewater in the presence of TiO_2 and/or FeCl_3 is possible; however, it was considerably slower than that in distilled water. The soluble components in the wastewater had a significant effect on the photodegradation rate of the SNs. Large concentrations of these contaminants (e.g., in landfill leachate) may inhibit the degradation process.

The combined use of TiO_2 and FeCl_3 , and a decrease in the pH of wastewater to ≤ 3 considerably accelerated the photocatalytic degradation of the SNs.

The main reasons for that phenomenon may be as follows:

- a decrease in the concentration of dissociated organic contaminants (in an acidic environment) originating from wastewater and intensification of the SNs adsorption on the TiO_2 surface,
- a decrease in the concentration of inorganic acid residues (in an acidic environment) with inhibitory properties,
- a reciprocal synergism of photodegradation processes initiated by TiO_2 and the product of FeCl_3 hydrolysis (mainly in the case of SMX).

In the case of the $\text{TiO}_2/\text{FeCl}_3$ mixture, increasing the FeCl_3 concentration $>1.5 \text{ mmol l}^{-1}$ caused an inhibition effect, whereas increasing the TiO_2 concentration in the range from 0.25 to 3.5 g l^{-1} increased the photodegradation rate of the SNs to only a small degree. The relationship between the rate of photocatalytic SNs degradation in wastewater and their initial concentration was consistent with the Langmuir–Hinshelwood theory.

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